Strategies for laser-induced fluorescence
detection of nitric oxide in high-pressure flames.
I. A–X(0,0) excitation

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Ronald K. Hanson

Three different high-pressure flame measurement strategies for NO laser-induced fluorescence (LIF) with A–X(0,0) excitation have been studied previously with computational simulations and experiments in flames up to 15 bars. Interference from O₂ LIF is a significant problem in lean flames for NO LIF measurements, and pressure broadening and quenching lead to increased interference with increased pressure. We investigate the NO LIF signal strength, interference by hot molecular oxygen, and temperature dependence of the three previous schemes and for two newly chosen excitation schemes with wavelength-resolved LIF measurements in premixed methane and air flames at pressures between 1 and 60 bars and a range of fuel/air ratios. In slightly lean flames with an equivalence ratio of 0.83 at 60 bars, the contribution of O₂ LIF to the NO LIF signal varies between 8% and 29% for the previous schemes. The O₂ interference is best suppressed with excitation at 226.03 nm. © 2002 Optical Society of America

1. Introduction
Detection of nitric oxide during combustion is of particular interest as NO is one of the most important combustion-generated pollutants. Automotive engines and gas turbines play a major role in the overall production of NO, which influences atmospheric ozone depletion and smog formation. In the future, drastic regulatory restrictions on NO release are expected. Despite use of catalytic converters for NO abatement, it is an important task to make engine exhaust cleaner. Imaging measurements during the formation of the pollutant within the combustion process have attracted much interest to aid the development of simulation models and to provide a tool for the optimization of practical combustion systems. Many of these practical devices operate at elevated pressures, and a strategy for quantitative laser-induced fluorescence (LIF) imaging of NO at pressures in excess of 50 bars is desired.

LIF can provide instantaneous two-dimensional images of absolute concentration fields without perturbing the process under investigation. Several studies have addressed NO imaging measurements in practical combustion processes such as high-pressure burners and gasoline and Diesel internal combustion engines. In further experiments, NO LIF imaging was used for temperature measurements and flow visualization. Different approaches for NO excitation have been previously suggested, including NO excitation in the D–X(0,1) band and several A–X vibrational bands. The literature does not give clear guidelines as to which transitions are favorable in a given diagnostic situation. We examined NO LIF excitation and detection strategies in premixed methane and air flames as a function of an equivalence ratio and pressures between 1 and 60 bars. Wavelength-dispersed LIF spectra are recorded versus excitation wavelength to select the optimum excitation features and fluorescence collection bandpass. Interference LIF is quantified for each of the strategies studied. In a series of papers, we will compare transitions in the A–X band and recommend the most appropriate excitation and detection strategies for high-pressure flames.
NO LIF. Here we examine excitation of five different regions of the NO A–X(0,0) band and determine the degree of interference LIF.

2. Problems

A. Transmission Properties

Electronic excitation of NO from sufficiently populated states requires short UV wavelengths around 193 nm in the D–X(0,1) band or at 226, 237, 248 nm for excitation in the A–X(0,0), (0,1), and (0,2) bands, respectively. In many high-pressure combustion systems, laser and signal attenuation have been reported to be major problems. Recent experiments showed that hot CO$_2$ and H$_2$O are the main contributors to absorption in this spectral range. These compounds exhibit broadband absorption behavior with cross sections increasing with temperature and decreasing with wavelength. This effect increases with pressure because of the increasing number density of absorbers.

Transmission properties therefore limit the NO detection strategy choice and often rule out the application of D–X excitation in the presence of hot combustion products at high pressures. Most experiments therefore focus on the A–X system using various detection strategies, exciting different rotational transitions in the (0,0) band as well as transitions in the (0,1) and (0,2) bands, which further reduce laser attenuation.

B. O$_2$ Laser-Induced Fluorescence Interference

The main concern when we choose a potential wavelength for NO excitation is the suppression of spectral overlap of excitation of other species that might result in an interfering LIF signal. Hot O$_2$ is the main contributor to LIF interference in lean and nonpremixed flames. The Schumann–Runge bands of O$_2$ overlap with the NO gamma bands over a wide range of excitation wavelengths resulting in the O$_2$ fluorescence signal overlapping with NO LIF. Measurements with spectrally resolved detection of the fluorescence light provide a way to distinguish between different signal contributions on the basis of their spectral signature. However, this approach is generally limited to zero- or one-dimensional measurements. For imaging measurements, bandpass filters are typically not suited to separate the overlapping signal intensities.

The ratio of O$_2$ LIF background increases with pressure for two reasons: variation in fluorescence quantum yield and variation in spectral overlap with the laser profile because of line broadening:

(i) The effective fluorescence lifetime of NO decreases linearly with pressure because of collisional quenching, whereas the effective fluorescence lifetime of excited O$_2$ is limited by its fast predissociation and is thus mostly pressure independent. Hence the relative fluorescence quantum yield and therefore the ratio of the O$_2$ and NO LIF signals increases with pressure.

(ii) As the pressure increases, the spectra are significantly altered by broadening and shifting. This increases the spectral overlap between NO and O$_2$ excitation, making the choice of excitation wavelengths more critical at high pressure. The line broadening also results in reduced spectral overlap of laser lines with the absorption features, which reduces the signal strengths. NO is much more affected by line broadening than O$_2$, again because of the fast predissociation of O$_2$. Therefore, with increasing pressure, the ratio of O$_2$ and NO LIF signals further increases.

C. Interference in Rich Flames

In rich and nonpremixed flames additional signal interference has been observed. Broadband fluorescence has been observed that is usually attributed to polycyclic aromatic hydrocarbons and partially burned hydrocarbons (aldehydes, ketones). This signal appears almost exclusively red shifted in respect to the laser wavelength. To avoid its detection, NO excitation from hot vibrational states, e.g., the (0,1) or (0,2) bands with subsequent detection of the blue-shifted NO fluorescence, has been suggested. In sooting flames at high laser energies, interference by LIF of laser-generated C$_2$ has also been reported. Its signal appears both red and blue shifted relative to the excitation laser and must be considered as an additional source of interference.

3. Background

In this paper and the following discussion we focus on the NO A–X(0,0) system at 224–227 nm only. Different strategies have been successfully used for NO measurements in premixed methane and air flames, heptane spray flames, and in internal combustion engines fueled with propane, low-sooting Diesel fuel, and commercial Diesel fuel. To minimize O$_2$ LIF interference, various transitions have been selected from simulation calculations of NO and O$_2$ LIF spectra and from measured spectra and their dependence on pressure, temperature, and equivalence ratio.

Cooper and Laurendeau, Reisel and Laurendeau, and Charleston-Goch et al. used the Q$_2$ transition at 225.58 nm for various high-pressure applications after spectroscopic investigations in the 1–15-bar range. Dec and Canaan and van den Boom et al. used the $P_1$($23.5$), $Q_1$ + $P_2$($14.5$), $Q_2$ + $R_{12}$($20.5$) feature at 226.03 nm for their in-cylinder Diesel engine measurements. This transition had been proposed earlier by Battles and Hanson on the basis of detailed spectroscopic investigations and studied in flames up to 10 bars by DiRosa et al. Bräumer and colleagues chose the $R_1$ + $Q_2$($21.5$) transition at 225.25 nm for their in-cylinder measurements based on simulation calculations.

Different strategies have been proposed for the assessment and correction of remaining O$_2$ LIF interference. Battles and Hanson, DiRosa et al., and Thomson and colleagues suggested an O$_2$ background correction based on the subtraction of an ad-
ditional LIF measurement off the NO resonance. Both groups suggested off-resonance excitation wavelengths close to the resonant NO line. At pressures >20 bars however, the NO spectra become so dense that a nonresonant excitation within the (0,0) band cannot be found (compare with Fig. 3). Dec and Canaan\(^5\) instead used an off-resonance wavelength of 227.503 that is far off the (0,0) band head at 227.01 nm to demonstrate that O\(_2\) fluorescence was not interfering in their measurements. Furthermore, because O\(_2\) LIF intensities are also strongly wavelength and pressure dependent, it cannot be assured that a measurement at a NO off-resonant position yields correct background intensities.

A different approach termed two-zone detection was proposed by DiRosa \textit{et al.}\(^{29}\) Here, the signal from O\(_2\) in a second spectral region exclusive of NO provides an indirect measure of the O\(_2\) interference in the NO detection bandpass. To our knowledge, application of this method has not yet been shown. Furthermore, in the 310–400-nm wavelength range, they suggest that, for O\(_2\) polycyclic background detection, strong LIF interference from partially burned combustion intermediates (Polycyclic aromatic hydrocarbons, aldehydes, ketones) must be expected in practical combustion situations.

In addition to the need for minimizing O\(_2\) LIF interference, different authors applied different criteria for the choice of excitation transition. Although Laurendeau and colleagues\(^{30–32}\) chose a line with minimized temperature sensitivity at combustion temperatures, Bräumer \textit{et al.}'s choice was limited by the available laser source; the 248-nm output of a KrF excimer laser is shifted to its first anti-Stokes wavelength at 226 nm in a 10-bar hydrogen cell to give sufficient laser energy (several millijoules) for imaging measurements.\(^5\) The tuning range of the excimer laser, however, limits the choice to rotational states with high ground-state energies.\(^{34}\) Dec and Canaan used a frequency-doubled optical parametric oscillator system,\(^5\) which could access the full (0,0) spectrum and provides high laser energies for imaging measurements. Cooper and Laurendeau's frequency-doubled dye laser system also provided broad wavelength tuning with sufficient laser energy because they performed only point measurements.\(^4\)

In the present study we compare the different NO A–X(0,0) excitation strategies in spectrally resolved LIF measurements in premixed methane and air flames with different air/fuel ratios in the 1–60-bar range. The candidate transitions are summarized in Table 1. In addition to the two transitions mentioned above, two new transitions with minimized O\(_2\) interference are investigated. These transitions were chosen to cover a large range of ground-state energies for use in a two-line or multiline technique for measurement of rotational temperatures. One of these transitions is within the tuning range of a Raman-shifted KrF excimer laser, providing an alternative choice when we use that laser system.

For the first time to our knowledge, comparisons of the candidates are made under well-defined conditions in terms of relative O\(_2\) interference in lean and stoichiometric flames as a function of pressure and equivalence ratio. In addition, we compare signal strength and temperature dependence. Significant differences lead to the result that one of the candidates is clearly superior to the others. Fluorescence quenching and energy transfer processes are not discussed here. In earlier experiments no dependence of these processes on rotational quantum numbers was found.\(^{35}\) Although playing an important role for quantitative evaluation of the NO LIF data, these processes can be omitted in this relative comparison.

Whereas this paper focuses on A–X(0,0), a similar comparison of promising transitions within the A–X(0,1) band is nearly completed.\(^{36}\) The comparison between transitions of different vibrational states including the influence of broadband interference in rich flames in under way.\(^{37}\)

### 4. Experiment

Laminar, premixed methane and air flat flames at pressures from 1 to 60 bars were stabilized on a porous, sintered stainless-steel plate of 8 mm in diameter; this burner was mounted in a stainless-steel housing with an inner diameter of 60 mm with pressure stabilization ±0.1 bar.\(^{38}\) Investigations were performed for fuel/air equivalence ratios of \(\phi = 0.83, 0.93, 1.03, \text{ and } 1.14\). All measurements were carried out with 300 parts per million NO seeded to the feedstock gases to mimic engine-like conditions. Optical access to the flame was possible by way of four quartz windows (Fig. 1).

Laser light (2 mJ at 224–227 nm, 0.4 cm\(^{-1}\) FWHM) from a Nd:YAG-pumped (Quanta Ray GCR250) frequency-doubled (\(\beta\)-barium borate) dye laser (LAS, LDL205) was aligned parallel to the burner surface and passed through the center of the flame 2 mm above the burner matrix. The pulse energy was

### Table 1. Investigated Transitions

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Transition</th>
<th>Excitation Wavelength</th>
<th>Ground-State Energy (\epsilon/k)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>High (T)</td>
<td>(R_1 + Q_{21}(26.5), Q_2 + R_{14}(34.5), P_1(40.5))</td>
<td>224.82</td>
<td>1750–4032</td>
<td>This paper</td>
</tr>
<tr>
<td>Sick</td>
<td>(R_1 + Q_{21}(21.5))</td>
<td>225.25</td>
<td>1161</td>
<td>6</td>
</tr>
<tr>
<td>Laurendeau</td>
<td>(Q_d(26.5))</td>
<td>225.58</td>
<td>1967</td>
<td>30</td>
</tr>
<tr>
<td>DiRosa</td>
<td>(P_1(23.5), Q_1 + P_{21}(14.5), Q_2 + R_{14}(20.5))</td>
<td>226.03</td>
<td>540–1381</td>
<td>28, 29</td>
</tr>
<tr>
<td>Low (T)</td>
<td>(P_2 + Q_{13}(1.5–4.5))</td>
<td>226.87</td>
<td>178–232</td>
<td>This paper</td>
</tr>
</tbody>
</table>
measured with a fast photodiode (LaVision). The beam was focused with a cylindrical lens to form a horizontal light sheet with a $3 \text{ mm} \times 0.5 \text{ mm}$ cross section. Fluorescence signals were collected at right angles to the laser beam and focused with $f = 105\text{-mm}$, $f/4.5$ achromatic UV lens (Nikon) onto the horizontal entrance slit of a $250\text{-mm}$ imaging spectrometer (Chromex 250IS) equipped with a $600$-grooves/mm grating. The dispersed fluorescence signals were detected with an intensified CCD camera (LaVision FlameStar III). Each laser pulse yielded a complete fluorescence spectrum maintaining one-dimensional spatial resolution along the laser light path.

The laser was tuned to record excitation spectra around the five candidate transitions, each scan covering $\pm 0.013 \text{ nm}$ in steps of $0.001 \text{ nm}$. The signal was averaged over $20$ laser pulses for each excitation wavelength and stored for further evaluation before the laser was scanned to the next wavelength. The $20$-shot averaged spectra were corrected for variations in laser-pulse energy.

5. Results and Discussion

We present the results for the investigation of the five candidate transitions within the A–X(0,0) band. For clarity, the transitions used in the literature are hereafter assigned the names Sick, Laurendeau, and DiRosa as defined in Table 1; having in mind a possible application for thermometry, the two new transitions starting from levels with low and high ground-state rotational energies are called low $T$ and high $T$, respectively.

The camera initially detects images with the spatial resolution along the horizontal path of the laser beam through the flame on one axis and spectral resolution showing emission spectra on the second axis. Two of these images are shown in Fig. 2(a) for typical situations in a lean $60\text{-bar}$ flame with DiRosa and Sick excitation, respectively. The central area of the flame, where temperature and concentrations are homogeneous, is then chosen (marked by the lines in Fig. 2) and integrated over the spatial axis producing the resolved fluorescence spectrum shown in Fig. 2. Each of these spectra becomes a single line in the two-dimensional excitation fluorescence chart shown in Fig. 2(b). After we scan the excitation laser on wavelength the next line is recorded and added to the two-dimensional chart. The resulting two-dimensional excitation and emission charts show excitation and fluorescence wavelengths on the opposite axis with the intensity values shown as a gray scale. This representation contains the full spectral information and allows later evaluation of excitation as well as emission spectra with an arbitrarily selected bandpass. Note that the interference from $\text{O}_2$ LIF at the Sick excitation is evident in the resolved fluorescence shown in Fig. 2(a). Profiles along the excitation frequency coordinate yields excitation spectra, where the bandpass of the detection can be selected.
arbitrarily over the entire fluorescence range. Similarly, fluorescence spectra can be extracted with the excitation frequency fixed at a given value.

Figure 2 gives an example for a two-dimensional spectrum near the Sick transition for 40 bar and 0.83. Note the difference in the scale of the excitation and emission wavelength axis. The strong emission signal at 225 nm is due to elastically scattered laser light. Emission from the NO A–X(0,0) band also contributes to this signal. The vibrational progression of the NO fluorescence in the A–X band can clearly be seen and is easily distinguished from the vibrational progression of the interference O₂ B–X fluorescence.

A. Excitation Spectra
We extracted fluorescence excitation spectra by plotting the signal in the 4-nm bandpass centered on the wavelength of the maximum of the NO A–X(0,1) emission (236 nm) versus the excitation wavelength. Figure 3 shows spectra around the five candidate transitions for all pressures investigated for the slightly lean (φ = 0.93) flame. The contribution of O₂ LIF to the emission is small in this fluorescence bandpass (see Subsection 5.D).

Collisional line broadening and shifting has been investigated in detail for the NO molecule. Its effect can be clearly seen in Fig. 3 as the peak signal shifts to longer excitation wavelengths with pressure. At the same time, line broadening becomes significant and smears out the rotational structure for pressures >10 bar. For all investigated transitions, the peak signal strength increases slightly between 1 and 5 bars and then decreases again for increasing pressure. As we discuss in subsections 5.B–5.D, this variation in signal strength is due to the combined effects of varying excitation efficiency, fluorescence yield, and NO number density. The discussion focuses on comparisons of the different excitation schemes for various flame conditions.

B. Emission Spectra
Fluorescence emission spectra are extracted from the excitation and emission maps as horizontal profiles from the two-dimensional excitation and emission charts. The laser is tuned to the NO LIF peak maximum for each individual pressure for pressures of 1–20 bars. Because of the loss of distinct peaks at higher pressures, the positions of the peaks at 20 bars are also used for the measurements of 40 and 60 bars. Only a limited number of these spectra are shown to demonstrate their typical behavior. Further data reduction leads to the more compact information presented below.

Figure 4 shows emission spectra between 220 and 290 nm for the five candidate transitions in the p = 40 bar and φ = 0.83 flame. Dominant features are the Rayleigh signal at the 224–227 nm excitation wavelengths and the NO fluorescence in the A–X(0,1)–(0,5) bands at 237, 247, 259, 272, and 285 nm, respectively. The relative intensities of the NO
emissions reflect the Franck–Condon coefficients,\textsuperscript{39} convoluted with the collection efficiency of the spectrometer and camera system that has a maximum at approximately 280 nm. Especially for the Sick and the Laurendeau transitions, the vibrational progression of the O\textsubscript{2} fluorescence is also visible. The purity of the NO signal in terms of O\textsubscript{2} interference and the NO signal strength is qualitatively observed from such spectra. The interference and signal strength can be quantitatively compared by use of a multiple Gaussian fitting technique described in Subsection 5.

C. NO Signal Strength

The influence of pressure and the equivalence ratio on the NO and O\textsubscript{2} LIF emissions is shown in Fig. 5 for the Sick transition. Emission spectra are shown for \( p = 5, 20, \) and 60 bar, \( \phi = 0.83, 0.93, 1.03, \) and 1.14. Relative O\textsubscript{2} LIF interference increases with increasing pressure and decreasing equivalence ratio. It should be mentioned that the O\textsubscript{2} LIF contribution disappears in the rich flames. In the rich flames with increasing pressure, the NO signal disappears faster than in the lean flames. Here, the NO added to the fresh gases is affected by NO reburn reactions. These reactions are known to be much more efficient in rich flames.\textsuperscript{40–42}

C. NO Signal Strength

The relative contributions of NO and O\textsubscript{2} LIF were evaluated with a nonlinear least-squares fit of multiple Gaussian line shapes to separate the overlapping NO and O\textsubscript{2} signals. A detection bandpass range from 230 to 253 nm was chosen, which includes the NO A–X(0,1) and (0,2) bands as well as three O\textsubscript{2} B–X bands. This represents the most important bandpass for NO detection for practical applications (imaging as well as pointwise detection) because of the large Franck–Condon factors of the NO (0,1) and (0,2) bands,\textsuperscript{39} which provide strong signals and maximum NO/O\textsubscript{2} LIF ratios. Best-fitting results could be achieved by use of a single Gaussian for each O\textsubscript{2} emission peak (O\textsubscript{2} transitions had sufficiently low rotational quantum numbers) and two Gaussians for each NO emission peak that account for a broader and bimodal NO emission feature.\textsuperscript{42} Figure 6 shows the results of the fitting algorithm for the \( p = 40 \) bar, \( \phi = 0.83 \) flame with the Laurendeau excitation. NO and O\textsubscript{2} signal strengths are evaluated by integration of the respective Gaussian fits.

The total NO signal strengths in the bandpass region from 230 to 253 nm for the investigated flames are shown in Fig. 7. For a given flame condition (in terms of pressure and equivalence ratio) the absolute NO and O\textsubscript{2} number densities as well as the temperature are identical for all candidates, enabling a direct relative comparison. Figure 7 reveals a large difference in signal strengths for the different candidates. Generally, transitions that consist of multi-
ple overlapping lines (like the DiRosa, high $T$, and low $T$ features) give higher signal intensities.

A change in flame conditions also changes temperature, number densities, and NO reburn chemistry, thus affecting NO and O$_2$ LIF signals. A comparison of signal intensities for different flame conditions as well as a comparison of measured and simulated signal strengths is therefore not possible on the present stage. This will be included in forthcoming research including measurements of absolute NO concentrations and temperatures. Nevertheless, on the basis of calculations and experiments, it can be assumed that, in the lean flames, reburn reactions lead to a $<10\%$ uncertainty in local NO concentrations.

An optimized strategy for NO detection should involve excitation of the transition at maximum signal strength as a function of pressure. This, however, is not possible in environments with fluctuating pressure (e.g., internal combustion engines). In that case a compromise must be found between signal strength and investigated pressure range. Because of the simultaneous action of pressure broadening and shift, signal variation for a given excitation wavelength is most pronounced for pressures between 1 and 5 bars and much less for higher pressures. For applications with pressures $>5$ bars we propose using an excitation wavelength at the 5-bar peak. For applications with lower pressure (1–5 bars), the 1-bar peak should be used. This, however, reduces the signal strength at higher pressures.

The pressure influence on NO LIF intensities was simulated on the basis of a four-level model. We calculated NO transition frequencies and rotational line strengths using relations from Paul. Vibrational transition probabilities were taken from Laux and Kruger, and pressure-broadening and pressure-shifting coefficients of NO from DiRosa and Hanson as well as Vyrodov et al. Calculations were carried out for the laser line width of our system of 0.4 cm$^{-1}$ FWHM and additional line widths of 0.5 and 0.25 cm$^{-1}$, respectively, typical for the Raman-shifted tunable excimer system and the optical parametric oscillator system.

In Fig. 8 the resulting calculated pressure dependence is shown for the DiRosa and the Sick lines. The upper plots assume the tuning to the NO LIF peak maximum for each pressure. Only for pressures $\leq 5$ bars does the laser linewidth influence the LIF signal; at higher pressures, broadening of the NO transitions becomes dominant. The lower curves show the relative loss in signal when a single laser wavelength is used throughout the entire pressure range. Tuning the laser to the NO LIF maximum at 1 bar leads to an increased pressure sensitivity in the intermediate pressure range (10–40 bars), whereas tuning the laser to the 10-bar maximum leads to signal loss at low pressures ($<5$ bars). Reduced overall pressure sensitivity is achieved when the laser is tuned to the NO LIF maximum at 5 bars. Figure 8 also shows that pressure variations are more severe with narrow-band lasers. The overlap of the multiple lines of the DiRosa transition leads to a broad excitation feature even at low pressures, strongly reducing pressure sensitivity in the $p = 1$–5 bar range in comparison with the Sick transition.

D. Oxygen Laser-Induced Fluorescence Background

The O$_2$ LIF background is also assessed from the Gaussian fits. Figure 9 shows the ratio of O$_2$ emission to the total emission of NO plus O$_2$ for all five candidate lines. The error bars represent the uncertainties that are due to the fitting algorithm. As discussed qualitatively in Sub section 5.B, O$_2$ interference generally increases with increasing pressure and decreasing equivalence ratio. The latter is simply an effect of an increasing O$_2$ number density in the exhaust gases of lean flames. Indeed, for the slightly rich $\phi = 1.03$ flame, the O$_2$ LIF signal is almost not visible (compare with Fig. 5). The data in Fig. 9 are shown for equivalence ratios of $\phi = 0.83$ and 0.93. In the $\phi = 1.03$ and 1.14 flames as well as for all equivalence ratios at 1 bar, O$_2$ LIF signals were too weak to measure.

The five candidate transitions were chosen to effectively suppress O$_2$ interference. Still, from Fig. 9 a surprisingly large difference between the candidates becomes evident. Although excitation of the Laurendau and Sick transitions leads to strong O$_2$ interference (up to 29\% for the highest pressure and lowest equivalence ratio investigated), excitation of
the DiRosa transition under the same conditions reduces the interference to ≤8%. This excellent performance is due to both the high NO signal strength (as discussed in Sub section 5. C) as well as the low O₂ LIF contribution. Note that Bräuner et al.⁶ could access only a limited range of transitions with their Raman-shifted tunable KrF excimer laser. The high-T transition is an alternative line within the tuning range of that laser system. With an interference of only 16% for the worst-case condition, the high-T transition has a clear advantage over the Sick transition. With ≥15% O₂ LIF interference, the low-T transition provides an intermediate performance.

The present data were evaluated for a rectangular detection bandpass of 242 ± 11 nm. We can further reduce the O₂ LIF interference by applying a narrower detection bandpass, e.g., only around the NO (0,1) or (0,2) emission with 236 ± 5 nm or 247 ± 5 nm, respectively. This leads to further suppression of the O₂ emission around 242 nm. For the p = 60 bar, φ = 0.83 flame with Sick excitation, this would reduce the O₂ interference from 26% to 17% or 20%, respectively, and for the Laurendeau excitation from 29% to 21% or 20%, respectively. At the same time the NO signal is reduced by a factor of 0.45 and 0.55 for (0,1) and (0,2) detection, respectively.

Measurements with DiRosa excitation show that O₂ interference stays below 8% and that therefore a background correction is not necessary even for lean (φ ≥ 0.83), high-pressure (p ≤ 60 bars) environments with NO concentrations of approximately 300 parts per million (which is comparable to concentrations present in internal combustion engines).⁷

E. Temperature Sensitivity

Quantitative NO concentration measurements without the exact knowledge of local temperature require one to choose a transition that minimizes the temperature sensitivity. Figures 10 and 11 show that there are significant differences for the five transitions; the main temperature influence comes from the ground-state population of the laser-coupled levels. The respective ground-state energies are listed in Table 1. For practical applications, however, further temperature-dependent effects have to be considered. Because line broadening and shifting is temperature dependent, the overlap of the spectral features with the spectral shape of the laser will also show temperature dependence.

Temperature also influences the fluorescence quantum yield by changing collisional frequencies and quenching cross sections. This influence is identical for all transitions in the same way because the quenching rates do not vary with rotational state for NO. Nevertheless, we included the resulting temperature dependence in the calculations using the Paul et al. models for quenching rate coefficients.¹⁷,⁴⁶ For simplification we make the assumption of complete combustion in a stoichiometric flame; thus only N₂, H₂O, and CO₂ colliders are included in the calculation. This assumption is valid for the present calculations because neither O₂ and CH₄ nor equilibrium OH that is formed from H₂O at elevated temperatures show a variation of quenching cross section with temperature for T > 1000 K.⁴⁶

Fig. 9. O₂ LIF contribution to the total NO plus O₂ LIF signal between 230 and 253 nm.

Fig. 10. Temperature dependence of the NO LIF signal for the number density. Stimulation for p = 10 bars.
transitions in the moderate temperature range and thus enables their use for quantitative measurements without temperature corrections. The results of this approach are shown in Fig. 11. The accessible regions with the Laurendeau and DiRosa lines thereby shift to low temperatures, whereas the LIF maxima of the high-T and the Sick lines are shifted to 1800 and 1500 K, respectively; however, their gradients become steeper.

F. Laser and Signal Attenuation
At the short wavelengths used here for NO detection, the transmission in high-pressure combustion environments is restricted. In our measurements near 225 nm, we find that at 60 bars the laser intensity decreases by 37% over the cross section of the flame (6 mm) (see also Fig. 2). This observation agrees well with calculations based on recently obtained absorption cross sections of hot CO2 and H2O. For 2000 K these data predict 40% and 4% absorption by CO2 and H2O, respectively. Laser attenuation by NO was negligible.

The distribution of CO2 in exhaust gases is usually reasonably well known. However, because CO2 absorption cross sections are strongly temperature dependent, additional information on local temperatures would be required for correction of light attenuation. For two-line or multiline temperature measurements, however, the CO2 absorption causes no additional problems. Because CO2 absorption cross sections show little dependence on wavelength variations of a few nanometers, local laser intensities can be considered identical for different excitation wavelengths within the A–X(0,0) band. Therefore the effects of CO2 absorption cancel out when temperatures are calculated from intensity ratios.

6. Summary
LIF measurements were performed for NO A–X(0,0) excitation in laminar, premixed methane and air flames between 1 and 60 bars with equivalence ratios between 0.83 and 1.14. Five different excitation strategies have been investigated and compared for feasibility of quantitative NO diagnostics in high-pressure flames. Of these five, the P1(23.5), Q2 + P21(14.5), Q2 + R12(20.5) (DiRosa) excitation feature at 226.03 nm shows the best performance in terms of minimizing molecular oxygen LIF interference as well as maximizing signal strength. The results show that even for lean (Φ ≤ 0.83) and high-pressure (p ≤ 60-bar) environments with NO seeding of approximately 300 parts per minute, O2 LIF interference is ≤8% for the DiRosa excitation. This transition offers clear advantages over the frequently proposed Q2(26.5) (Laurendeau) line at 225.58 nm that has an O2 LIF interference background as large as 29%.

The limited tuning range of a Raman-shifted tunable KrF excimer laser restricts the set of possible NO excitation transitions. We find here that the newly proposed R1 + Q21(26.5), Q2 + R12(34.5), P1(40.5) (high-T) feature at 224.82 nm significantly reduces
the O₂ LIF interference (≤16% for all investigated flames) in comparison with the previously used R₂ + Q₂₁(21.5) (Sick) transition at 225.25 nm (27% maximum O₂ LIF interference).

We also explored the possible excitation strategies for NO rotational thermometry. Investigations on the P₃₁ + Q₁₂(1.5–4.5) (low-T) transition at 226.87 nm with a low ground-state energy show an O₂ LIF background of <14% for all investigated flames. Together with the DiRosa and the high-T transitions, two- or three-line rotational thermometry should be feasible even in lean high-pressure environments.

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